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(54) **Alkaline primary battery with improved seal and method of manufacturing same.**

(57) The leakage of electrolyte from alkaline primary batteries is substantially reduced by improving the seal in such batteries. The novel seal is formed by applying a thin adherent plastic film to the surface of the metal container which forms a bond between the metal container and the sealant covered seal member normally used in such batteries.

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ALKALINE PRIMARY BATTERY WITH IMPROVED SEAL AND METHOD OF MANUFACTURING SAME.

The invention relates to alkaline primary batteries and, in particular, to theseal which prevents the leakage of electrolyte and a method of manufacturing such alkaline batteries.

Alkaline primary batteries and, in particular, alkaline manganese dioxide/zinc dry cells (MnO_2/Zn), have been a successful commercial development. When manufactured in a cylindrical configuration, the battery seal is typically made by compressing a plastic member within a metal can by crimping the open end of the can as disclosed by Ralston and KO in U.S. Patent No. 3 663 301. More particularly, the typical commercial use of this type seal employs a nickel plated steel can as the positive current collector, a plastic seal member, typically of nylon or polypropylene, and a sealant, such as bitumen, between the metal can and the plastic seal member. While such seals performs satisfactorily when the steel can is plated with nickel, if the steel can is unplated, such seals are very poor. The poor seals are probably due to differences in bond strength of butimen and steel and bitumen and nickel plated steel.

It is an object of the invention as defined in the appendent claims to provide for a stronger seal for alkaline cylindrical cell and a method of manufacture of such cell. Another object of the invention is to provide for strong seals in alkaline cylindrical cells wherein the metal cans, i.e., the positive current collectors are unplated steel.

A polymeric resin, which upon drying becomes a thin adherent plastic film, when applied to the surface of the metal can of an alkaline dry cell, in the area of the seal greatly improves the strength of the seal, thereby reducing leakage problems associated therewith.

The objects of the present invention are achieved by applying a polymeric resin to the surface of the metal container (positive current collector) in the area of the battery seal. The resulting thin plastic film forms a bond between the metal container and the sealant covered seal member, normally used in battery seals. By practicing the present invention, the positive current container can be unplated steel, which reduces the cost of manufacturing alklaine cylindrical cells.

In accordance with the present invention, the interior surface of the metal can of an alkaline dry cell is coated with a polymeric primer. This primer, which may be applied by various techniques, including painting, spraying or dipping, contains an alkaline resistant organic binder dissolved in a compatible solvent. Spraying is the preferred method of applying the organic primer.

After being applied to the metal can, the primer is dried at elevated temperatures, which permits the evaporation of the solvent and allows for the adhesion of a thin, resin coating to the metal container. The resulting coating is typically 0.0006" to 0.0008" (15 to 20 µm) in thickness, but may range from 0.0001" to 0.002" (25 to 50 µm) in thickness.

In the present invention, the binder is a film forming polymer which is compatible with alkaline battery components. Film forming binders which hydrolyze or oxidize in the presence of the electrolyte cannot be used in practicing the present invention. The present invention can be successfully practiced with a wide range of polymeric binders including ABS (acrylonitrile butadiene styrene), PVC (polyvinyl chloride), epoxies, fluorcarbons, nylons, polypropylene, polybutylene, polystyrenes and neoprenes. The present invention may also be practiced with binders which are rubbers and/or elastomers, such as, isobutylene, isoprene, chloroprene, polysulfide, ethylene propylene, chlorinated and chlorosulfonated polyethylene, fluorosilicone and propylene oxide. However, materials which are soluble in KOH, the usual electrolyte found in alkaline battery systems, such as CMC, should not be used in practicing the present invention.

The solvent portion of the resin must wet the surface of the metal container. It must also be compatible with alkaline battery components and with the binder. The present invention can be successfully practiced with solvents such as ethyl acetate, butanol, methyl ethyl ketone, methyl isobutyl ketone and paraffinic hydrocarbon liquids.

The polymeric resin, which may itself be conductive, may contain other ingredients such as fillers. Particularly, a non-conductive polymeric resin may contain small amounts of conductive filler materials such as carbon or metal powder.

When carbon is added as the conductive filler, the weight percent of carbon in the film after the evaporation of the solvent should be less than 40%. Increasing the amount of carbon, which reduces the amount of binder in the plastic film, decreases the mechanical integrity of the plastic film and increases the probability that the conductive film will not remain adhered to the surface of the metal container.

In order to provide the advantages disclosed herein the plastic film must be impervious to the alkaline electrolyte. Therefore, the plastic film must be continous in the area of the seal/sealant and metal container interface.

Figure 1 is a drawing of an alkaline cylindrical battery incorporating this invention.

Figure 1 is a drawing of an alkaline cylindrical battery constructed according to the present invention. The positive current collector, a drawn steel container 2, open on one end and about 0.010"(0,25 mm)thick, has a coating 14 applied to its interior surfaces. Two cathode annular rings 5, formed such that their outside diameters are greater than the inside diameter of the positive current collector, are forced into the positive current collector, forming a pressure contact therewith. A bead 10 is rolled into the container near the open end to support the sealing disk. A separator 4 and an anode 3 are placed inside of the cathode rings. A sealing disk 6 containing a negative current collector 1 is placed into the open end of the container and in contact with the bead. The open end of the container is crimped over the sealing disk thus compressing it between the crimp and the bead to seal the cell. An insulation washer 7 with a central aperture is placed over the crimped end of the cell such that the end of the negative current collector 1 protrudes through the aperture. A contact spring 8 is affixed to the end of the negative current collector 1. Terminal caps 9 and 13 are placed into contact with the contact spring 8 and the positive current collector 2, respectively, and an insulating tube 12 and steel shell 11 are placed around the cell and crimped on their ends to hold the terminal caps in place.

Examples of the utility of the present invention will now be explained.

Example 1

Three sets of adhesion test samples were prepared. The first set used a substrate of nickel-plated steel, the second set used a substrate of unplated steel, and the third set used a substrate of unplated steel coated with P-70 primer (a conductive resin of PVC and carbon black dissolved in solvent manufactured by Pervel Industries). On to each substrate a metal washer with a 0.5" (12,7 mm) diameter opening was placed and a molten bitumen, Pioneer 135 (Witco Chemical Corp.), was poured inside the washer. The 5/8" (15,9 mm) diameter head of a bolt was then placed on the molten bitumen. These samples were then arranged in a tensile testing machine so that the force required to separate the bitumen from the substrate could be measured. The results in Table I show that the bond stregth was improved by use of the P-70 primer. In Table 1, the failure mode designation indicates the location of the separation. Cohesive failure is desired as this indicates that the weakest point of the bond is within the bitumen sealant itself, not at the substrate surface.

Table 1

0°F (12,5°) Adhesion Test Using Pioneer 135 Bitumen

Substrate	Adhesion, lb/.5" dia.	(kg/mm dia.)	Failure Mode
Nickel plated steel	3.9	1,4	Cohesive
Unplated steel	2.4	0,8	Adhesive
P-70 primed, unplated steel	4.6	1,6	Cohesive

Example 2

Two sets of alkaline manganese D-size cells were constructed using unplated steel cans as the positive current collector. The cans for the first set of batteries were not treated, while the metal containers used for the second set of batteries had their inner surfaces sprayed with P-70 primer. Batteries were then manufactured identically from the two sets of cans according to Figure 1. The cells were leakage tested by subjecting them to a thermal shock cycle consisting of 8 hours at 130°F (55°C) followed by 16 hours at 0°F (-12,5°C) for a total of three cycles. The outer wrap of each cell, consisting of the two terminal caps, the paper insulating tube, the insulating washer, the contact spring and the steel shell were then removed, and the number of cells with leakage between the sealing disks and the metal cans were counted. The data shown in Table II indicates that the present invention greatly improves the seal in alkaline cylindrical cells.

Table II

Three 0°F - 130°F (-12,5°C - 55°C) Thermal Shocks

Can	Primer	% Leakage
Unplated steel	None	100%
Unplated steel	P-70	0%

From the results in the foregoing examples and the referenced drawing, it is evident that the alkaline primary cells of this invention are superior to conventional alkaline primary batteries. While the foregoing examples used the alkaline Mn_2O/Zn electrochemical system in a commercial cylindrical configuration, the present invention includes other alkaline electrochemical systems which use an electrolyte which is not corrosive to the positive current collector.

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Claims:

1. Alkaline electrochemical cell having a sealing means comprised of a sealant, especially bitumen, disposed between a metallic container(2), which functions as a positive current collector, and a plastic seal member (6), especially of polypropylene or nylon,
characterized in that
the interior surface of the metal container (2) is provided with an alkali-resistant plastic coating (14).

2. Alkaline electrochemical cell according to claim 1,
characterized in that
the metallic container (2) is unplated steel.

3. Alkaline electrochemical cell according to claim 1 or 2,
characterized in that
the plastic coating (14) is conductive.

4. Alkaline electrochemical cell according to claims 1, 2 or 3,
characterized in that
the plastic coating (14) contains conductive fillers, preferably carbon.

5. Alkaline electrochemical cell according to claim 4,
characterized in that
the carbon weight percent of the plastic coating ranges up to 40.

6. Alkaline electrochemical cell according to any of claims 1 to 5,
characterized in that
the plastic coating is 0.0001" to 0.002" (2.5 to 50 µm) preferably 0.0006" to 0.0008" (15 to 20 µm) thick.

7. Alkaline electrochemical cell according to any of claims 1 to 8, characterized in that
the plastic coating is provided only in the area where the seal/sealant and metal container contact.

8. Method of manufacture of an alkaline electrochemical cell according to claim 1,
characterized by comprising the following steps:
(a) coating the interior suface of a metallic container, especially of unplated steel, serving as the positive current collector with an alkaline-resistant, polymeric resin;
(b) drying the polymeric resin coating, thereby forming an alkaline-restistant plastic film on the surface of said metallic container;
(c) placing alkaline battery components within said metallic container; and
(d) sealing said alkaline cell by disposing a sealant, especially bitumen, between a plastic seal member, especially of polypropylene or nylon, and said metall container upon crimping the heretofore open end of said metal container.

9. Method according to claim 8,
characterized in that
the metallic container is coated with an alkaline-resistant polymeric resin comprising a polymeric binder dissolved in a solvent.

10. Method according to claim 9,
characterized in that
after coating the solvent is evaporated from the polymeric resin at elevated temperatures.

11. Method according to claim 19,
characterized in that
a polymeric binder is used which does not dissolve in alkaline electrolyte and not hydrolyzed or oxidized by alkaline electrolyte.

12. Method according to any of claims 9 to 11,
characterized in that
a solvent is used which wets the surface of said metallic container.

13. Method according to any of claims 9 to 12,
characterized in that
a conductive polymeric binder is used.

14. Method according to any of claims 9 to 13,
characterized in that
the metallic container is coated with a polymeric resin comprising a binder with added conductive fillers, preferably conductive carbon particles selected from the group consisting of acetylene black, carbon black and graphite as a conductive filler.

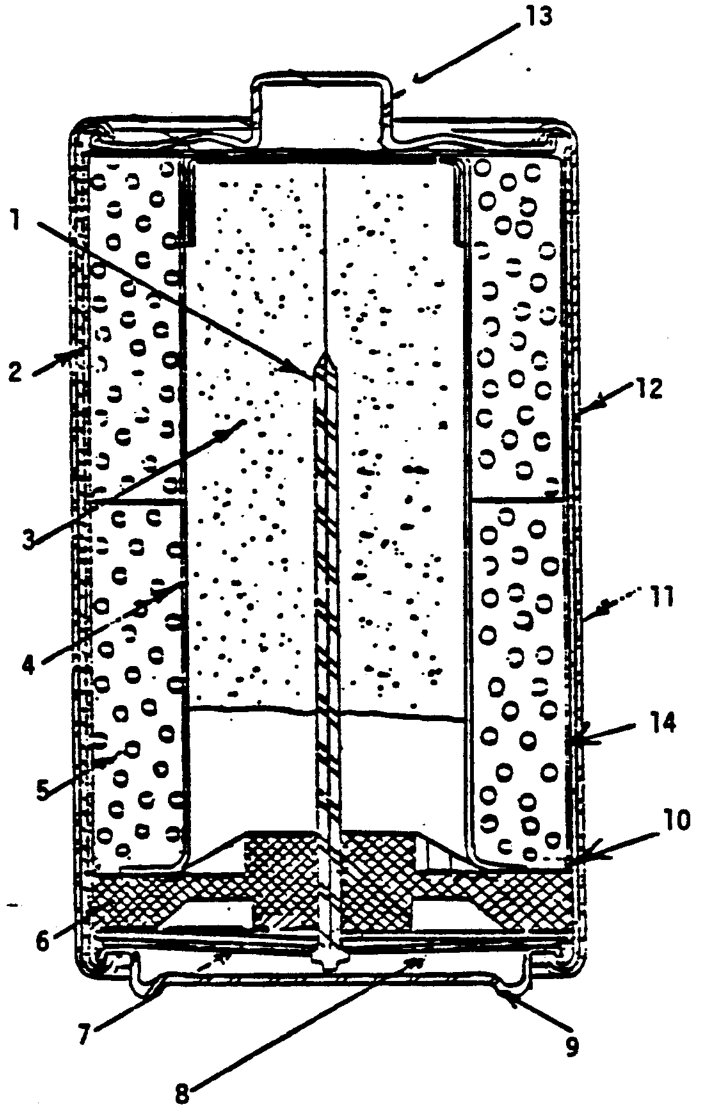
15. Method according to claim 13 or 14,
characterized in that
the metallic container is coated with a polymeric resin containing conductive carbon particles in such an amount that the weight percent of carbon in the plastic film ranges up to 40.

16. Method according to any of claims 8 to 15,
characterized in that
the polymeric resin is applied to the metal container only in the area where the seal/sealant and metal container contact.

17. Method according to any of claims 8 to 16,
characterized in that
the polymeric resin is applied to the metallic container in such an amount that the plastic film is 0.0001" to 0.002" (2.5 to 50 µm), preferably 0.0006" to 0.0008" (15 to 20 µm) thick.

FIGURE

ALKALINE CELL



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